Int J Life Cycle Assess (2009) 14:313–327
DOI 10.1007/s11367-009-0084-6

A characterization model with spatial and temporal resolution for life cycle impact assessment of photochemical precursors in the United States

Viral P. Shah · Robert J. Ries

Received: 5 December 2008 / Accepted: 22 March 2009 / Published online: 19 May 2009

Abstract
Background, aim, and scope Traditional life cycle impact assessment methodologies have used aggregated characterization factors, neglecting spatial and temporal variations in regional impacts like photochemical oxidant formation. This increases the uncertainty of the LCA results and diminishes the ease of decision-making. This study compares four common impact assessment methods, CML2001, Eco-indicator 99, TRACI, and EDIP2003, on their underlying models, spatial and temporal resolution, and the level at which photochemical oxidant impacts are calculated. A new characterization model is proposed that incorporates spatial and temporal differentiation.
Materials and methods A photochemical air quality modeling system (CAMx-MM5-SMOKE) is used to simulate the process of formation, transformation, transport, and removal of photochemical pollutants. Monthly characterization factors for individual US states are calculated at three levels along the cause–effect chain, namely, fate level, human and ecosystem exposure level, and human effect level.
Results and discussion The results indicate that a spatial variability of one order of magnitude and a temporal variability of two orders of magnitude exist in both the fate level and human exposure and effect level characterization factors for NO_x. The summer time characterization factors for NO_x are higher than the winter time factors. However, for anthropogenic VOC, the summer time factors are lower than the winter time in almost half of the states. This is due to the higher emission rates of biogenic VOCs in the summer. The ecosystem exposure factors for NO_x and VOC do not follow a regular pattern and show a spatial variation of about three orders of magnitude. They do not show strong correlation with the human exposure factors. Sensitivity analysis has shown that the effect of meteorology and emission inputs is limited to a factor of three, which is several times smaller than the variation seen in the factors.
Conclusions Uncertainties are introduced in the characterization of photochemical precursors due to a failure to consider the spatial and temporal variations. Seasonal variations in photochemical activity influence the characterization factors more than the location of emissions. The human and ecosystem exposures occur through different mechanisms, and impacts calculated at the fate level based only on ozone concentration are not a good indicator for ecosystem impacts.
Recommendations and perspectives Spatial and temporal differentiation account for fate and transport of the pollutant, and the exposure of and effect on the sensitive human population or ecosystem. Adequate resolution for seasonal and regional processes, like photochemical oxidant formation, is important to reduce the uncertainty

Responsible editors: Michael Hauschild and José Potting

Electronic supplementary material The online version of this article (doi:10.1007/s11367-009-0084-6) contains supplementary material, which is available to authorized users.

V. P. Shah
Department of Civil and Environmental Engineering,
University of Pittsburgh,
949 Benedum Hall,
Pittsburgh, PA 15213, USA

R. J. Ries (✉)
M.E. Rinker, Sr. School of Building Construction,
University of Florida,
304 Rinker, P.O. Box 115703, Gainesville, FL 32611, USA
e-mail: rries@ufl.edu

in impact assessment and improve decision-making power. An emphasis on incorporating some form of spatial and temporal information within standard LCI databases and using adequately resolved characterization factors will greatly increase the fidelity of a standard LCA.

Keywords Characterization model · LCA sophistication · Spatial resolution · Temporal resolution · Tropospheric ozone

1 Background, aim, and scope

The life cycle of a product or service consists of several processes which do not usually occur at the same points in space or time. The location and time of emissions strongly affect the fate of pollutants and also their impacts on the receptors. Traditional life cycle impact assessment (LCIA) methods have failed to account for the variation in impacts due to the location or the time of emissions (Potting and Hauschild 2006). They provide a single characterization factor for each substance in an impact category. Some of these factors are valid globally (e.g., global warming potential) while others are representative of the conditions in a particular country. While spatially distinguishing characterization factors are not applicable to impact categories that are global in scope, they add more certainty to regional impacts like photochemical oxidant formation. The uncertainty associated with using site and time generic factors can have a significant effect on the conclusions of the life cycle assessment (Potting and Hauschild 2006).

Potting and Hauschild (2006) have identified three levels of sophistication in spatial resolution of characterization factors, namely, site generic, site dependent, and site specific. A site-generic characterization factor does not consider any spatial differentiation in sources or the receiving environment. A site-dependent factor spatially differentiates the sources and their subsequent receiving environments. Source categories are defined at a spatial scale of countries or states within countries. Receiving environments are defined at a higher resolution (typically less than 150 km). Thus, site-dependent characterization factors include variation within and between the receiving environments with respect to each source category. They are also informed by background concentrations of pollutants in the receiving environments, and any thresholds in the concentration–effect relationship. In a site-specific characterization factor, only a few sources are considered, and the effects are modeled on receiving environments that are very close to the sources. This level of sophistication does not usually add significantly to the accuracy of the results. Therefore, the site-dependent level is the preferred level of spatial resolution for LCIA (Potting and Hauschild 2006). This does not invalidate site-generic LCA, but recognizes the value of time, location, and intensity of emission releases in evaluating impact. It has been argued that spatial differentiation in LCA adds an additional burden on the LCI data collection without adding significantly to the decision-making process. Bellekom et al. (2006) demonstrated that it is feasible and relatively easy to determine the LCI at the site-dependent level. Potting and Haushild (2005) have demonstrated that the differences in characterization factors among emission sites are larger than the differences in characterization factors between pollutants in both the acidification and photochemical oxidant formation impact categories. Recent LCIA methods, like TRACI (Bare et al. 2003) and EDIP2003 (Hauschild and Potting 2005), incorporate spatially resolved characterization factors for the regional impacts in the US and Europe, respectively.

Traditional LCIA methods integrate the emissions over the entire life cycle of the product or process. Therefore, all emissions are treated as a pulse rather than a flux distributed over a period of time. The debate on temporal differentiation within LCIA has focused on two separate topics. The first is the time horizon of impacts and the treatment of present and future emissions. For example, global warming potentials can be calculated for different time periods. Choosing any one period cuts off all future impacts that may potentially occur. The second is the importance of the calendar time of the emissions. Potting and Haushild (2005) have demonstrated the variation in the characterization factors for different years. This variation is due to the difference in the level of economic activity and emission control measures which affect the environmental concentration of the pollutants and the background exposure at the receptor sites. However, the seasonal variation in the impacts has been neglected in LCIA. Important environmental phenomena, like photochemical oxidant formation, acidification, and eutrophication, show large seasonal variability due to the processes responsible for fate and transport of the pollutants, and also due to the seasonal changes in the characteristics of the receiving environment.

This study compares four common impact characterization methods for photochemical oxidant formation and proposes a new model (Shah 2008) that addresses the limitations of spatial and temporal resolution in these methods. The four LCIA methods compared are: CML2001 (Guinée et al. 2002), Eco-indicator 99 (Goedkoop and Spriensma 2001), TRACI (Bare et al. 2003), and EDIP2003 (Hauschild and Potting 2005). Previous comparisons have been presented by Udo de Haes et al. (2002) and Pennington et al. (2004).

2 Photochemical oxidant formation

Photochemical oxidant is a mixture of atmospheric pollutants like tropospheric ozone (O_3) and other short-lived compounds like peroxyacetyl nitrate (PAN) and hydrogen peroxide. It is formed due to the photochemical reactions of oxides of nitrogen (NO_x) and volatile organic compounds (VOC), which are known as O_3 precursors. VOCs are oxidized by the hydroxyl radicals to form peroxides. The peroxides oxidize nitrous oxide (NO) in the atmosphere to nitrogen dioxide (NO_2). NO_2 is photolyzed to NO and an oxygen atom, which combines with O_2 to produce O_3.

NO_x is primarily emitted during combustion processes. Lightning, soil, and oceans are biogenic sources of NO_x. VOCs are emitted from automobiles and solvent evaporation from industrial and domestic applications. Many kinds of organic compounds volatilize from the leaves and branches of plants and trees, and biogenic sources are significant for VOCs.

In addition to the concentration of precursors, the concentration of O_3 at a particular location is dependent on meteorological conditions like intensity and spectral distribution of solar radiation, ambient temperature, and humidity. Long-distance transport through advection and diffusion, both in the horizontal and vertical directions, affects the concentration of O_3 and its precursors. O_3 concentrations change non-linearly with the concentration of its precursors. In low NO_x and VOC areas, O_3 concentration is directly related to the NO_x and VOC concentrations. However, at very high NO_x concentrations, found typically in dense urban areas, there is a net destruction of O_3 by reaction with NO. O_3 and its precursors are removed from the atmosphere through the processes of wet and dry deposition.

Photochemical Air Quality Modeling Systems (PAQMS) have been widely used to model the physical and chemical processes underlying tropospheric O_3. Based on their respective spatial representation, PAQMS can be divided into Lagrangian and Eulerian models. Lagrangian and Eulerian models employ two different frames of reference for the dynamics of atmospheric pollutants. In a Lagrangian model, the observer's reference frame moves along with the wind flow. Thus, the observer follows a parcel of air for a long period. In the Eulerian model, the reference frame is fixed to the earth or any stationary object. The earth's atmosphere is divided into grids and air parcels are transported from one grid cell to another with the flow of air and diffusion. Eulerian models have been preferred in recent years due to fewer assumptions in their formulation and the increase in computing power (Russell 1997).

A PAQMS has three core components which model different physical or chemical processes. Figure 1 illustrates the processes modeled by the chemistry and transport module, and the variables supplied by the meteorology and the emissions modules. The Chemistry and Transport model is the heart of the PAQMS. It simulates the processes of emission, chemical reaction, dispersion, and removal of the pollutants from the troposphere. It is based on the Eulerian continuity equation for gases, which has been modified to reflect key atmospheric processes. The equation relates the rate of change of the pollutant's concentration to the effects of convective transport, turbulent diffusion, chemical reaction, and emission or deposition of the species (Russell 1997). The meteorology model generates gridded meteorology fields which are essential for the processing of emission rates, chemical transformation, and species transport. Emission models process specific data inventories to derive estimates of hourly emissions of NO_x, CO, and several VOCs. They use surrogates, like population or land area, to generate emissions at the model grid resolution from the data inventories which are typically available at state or county level in the US. Temporal profiles are applied to derive hourly emission rates from coarsely resolved activity datasets.

Exposure to tropospheric O_3 is a cause of several respiratory and cardiovascular health effects, and even mortality in humans. Plants and ecosystems are adversely affected due to interference in photosynthesis and tissue damage from exposure to high O_3 concentrations. Ozone has an influence on ground-level UV radiation, thus affecting UV-related health outcomes. It is a greenhouse gas and contributes to global warming. Ozone has an indirect forcing effect due to its chemical interrelation with methane, NO_x, non-methane hydrocarbons, and CO. Man-made materials such as elastomers, fibers, dyes, and paints are known to be damaged by exposure to O_3. An overview of four common ozone impact assessment methods is presented below. A detailed discussion is presented as Electronic supplementary material.

3 Impact characterization of photochemical ozone

CML2001 Guinée et al. (2002) recommend the use of the Photochemical Ozone Creation Potential (POCP) metric as the characterization factor for NO_x and VOC emissions. POCP is defined as the increase in the amount of O_3 formed due to a unit increase in the emission of a particular precursor. The POCP values under western European conditions for NO_x and 95 VOCs have been calculated by Derwent et al. (1996) using a Lagrangian photochemical model. The simulation consisted of a base case scenario and several alternate scenarios in which the emission of each precursor was increased marginally. In the base case, the emission rates represented the worst case scenario in

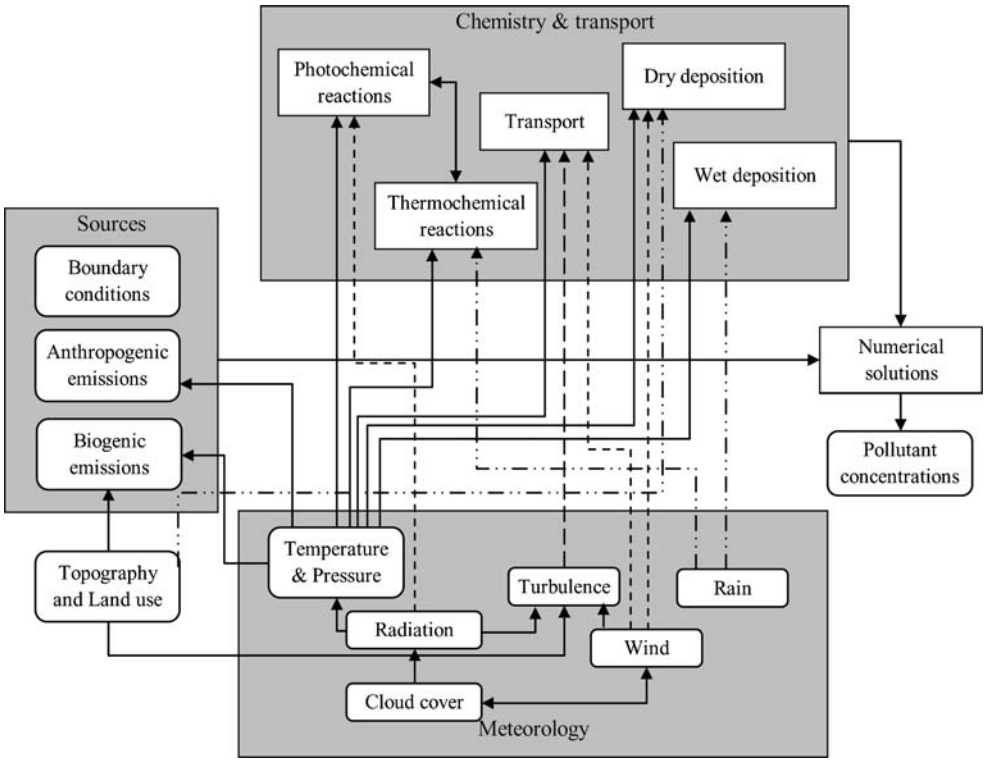

Fig. 1 Schematic representation of relationship between variables and processes of a PAQMS (adapted from Russell 1997)

northwestern Europe. POCP values for 101 VOCs have also been calculated under highly polluted North American urban conditions (Derwent et al. 2001). In EDIP97, Haushild and Wenzel (1998) have used the POCP values as characterization factors. However, they recommend the use of two different sets of POCP values, one for high-NO_x conditions and the other for low-NO_x conditions. High-NO_x condition POCP values have been obtained from Derwent and Jenkin (1991), and the low-NO_x condition values from Andersson-Sköld et al. (1992). Since POCP is a measure of the amount of the additional O_3 formed, it describes the impact at the category midpoint. The CML2001 method does not consider any spatial or temporal differentiation.

Eco-indicator 99 The photochemical oxidant formation impact in the Eco-indicator 99 method (Goedkoop and Spriensma 2001) is based on the endpoint method developed by Hofstetter (1998). The endpoint impact is the potential burden of an emission on an organism or area of concern typically in a primary area of protection such as human health, natural environment, or man-made environment. Midpoint impacts are calculated at intermediate levels in the cause–effect chain. The characterization factor is a product of fate and effect factors. The fate factors are based on the results of the simulations of the Lagrangian EMEP O_3 model reported by Simpson (1993). Base case simulations were performed for the summers (April to September) of 1985 and 1989. Three additional emission control scenarios were simulated for the 1989 summer. The fate factor for NO_x and VOC is the reduction in the mass of O_3 formed per unit decreases in precursor emissions. The effect factors are calculated from several epidemiological studies which describe the relationship between the various endpoints and an increase in ambient O_3 concentration. Eco-indicator 99 does not provide impact factors that are spatially or temporally differentiated. The characterization factors are calculated for average European conditions and do not represent the impact of photo-oxidant formation in other countries. The characterization factors are calculated at several endpoints of O_3 exposure. The DALYs (Disability Adjusted Life Years) index, which is the sum of life years lost due to mortality and morbidity, characterizes the human health area of protection at a fundamental level and can be easily comprehended by both scientists and policy makers.

TRACI The TRACI method has been specifically developed for North American conditions. It characterizes impacts at the midpoints to avoid the uncertainties associated with effect modeling. The characterization factors for most of the local and regional impacts have been calculated at the state level (Bare et al. 2003; Norris 2003). The category indicator for the impact is expressed in terms of grams of NO_x equivalents. It is based on the observation by Kasibhatla et al. (1998) of a near linear relationship between regionally accumulated O_3 concentra-

tion and NO_x emissions during summer O_3 episodes characterized by stagnant meteorological conditions. The state level characterization factors are calculated using state level NO_x source–receptor matrices developed by Shannon (1991) based on the ASTRAP model. ASTRAP was developed for simulating acid precipitation and does not include the photochemical reactions underlying the formation of O_3. The NO_x-equivalency factor of 2 for VOCs is calculated based on empirical data and modeling studies. It assumes that the transport and deposition characteristics for NO_x and VOC are identical and can be described by an NO_x source–receptor matrix. The Maximum Incremental Reactivity (MIR) scale of Carter (1998) is used to differentiate between the relative influences of VOC species on O_3 formation. The single-cell Empirical Kinetic Modeling Approach (EKMA) developed by the USEPA is used in the calculation of MIR. The MIR scenario is derived by adjusting the NO_x concentration in the base case scenario such that a small addition of the base VOC mixture will result in the maximum O_3 formation. The incremental reactivity is the increase in the mass of O_3 formed for a unit of additional mass of each VOC species to the modified NO_x scenario. Hence, MIR represents the potential of O_3 formation in high NO_x concentrations that are typically seen in highly polluted urban conditions. The characterization factors calculated in TRACI are spatially differentiated at the state level.

A limitation of the TRACI method is the use of two disconnected models (ASTRAP and MIR) to represent the transport and fate of the precursors, respectively. Additionally, the relative efficiency of O_3 formation of NO_x to that of VOC is based on a limited number of studies, and its spatial variability is also not considered. MIR values are based on highly polluted urban conditions and do not represent the average conditions prevalent throughout the year. An integrated approach, which is now available with the development of the PAQMS, can increase the sophistication of the O_3 modeling by addressing these limitations.

EDIP2003 The characterization factors for all non-global impact categories in EDIP2003 are resolved spatially at the country level for Europe. For photochemical oxidant formation, acidification, and terrestrial eutrophication, multiple sets of temporally differentiated characterization factors have been calculated (Hauschild and Potting 2005). The characterization factors have been calculated for 1990, 1995, and 2010 based on past emission inventories and the emission reduction plans for future years (Potting and Haushild 2005). The Regional Air Pollution Information and Simulation (RAINS) model has been used to generate the photochemical oxidant formation characterization factors for each country. The RAINS model relates the emission of precursors in any country to the concentration of O_3 in the boundary layer at the receptor site. It is a reduced-form model derived from multiple simulations of the Lagrangian EMEP model (Potting and Haushild 2005; Heyes et al. 1996, 1997). The exposure of humans and vegetation to tropospheric O_3 has been considered in the EDIP2003 method. The AOT40 index is used to calculate the vegetation exposure. AOT40 is the cumulative exceedance of the hourly daytime O_3 concentration above the 0.040 ppm (40 ppb) threshold level for the growing season. Since no thresholds for chronic exposure of humans to O_3 have been identified, AOT60 has been used. The EDIP2003 method follows an 'only above threshold' approach to impact assessment rather than a 'less is better' approach (Potting and Haushild 2005). In this approach, only the entities that experience exposures higher than the critical levels are valued. Due to the discontinuous nature of the threshold exceedance impact function, entities that are exposed only slightly less than the critical level and are at the maximum risk are completely neglected. A 'less is better' approach would value all entities equally, irrespective of their background exposures. Thus, reducing the exposure for an entity exposed high above the threshold would not have any additional preference over reducing the exposure for an entity exposed to very low levels. Currently, there is no general consensus in the LCIA community on which one of the two approaches is better.

The spatially differentiated human and vegetation impact characterization factors for NO_x and VOC showed a variability of two and four orders of magnitude, respectively. This reinforces the need for spatial resolution in the characterization of photo-oxidants. The average characterization factor for NO_x is three times that of VOC. The POCP approach used in the Eco-indicator 99 method is also recommended in EDIP2003.

3.1 Comparison of characterization methods

This study developed a new characterization model that addresses the limitations of the common characterization methods described above. Table 1 summarizes the key features of the four common methods and the proposed method (Shah 2008). In CML2001 and TRACI, the impact factors are calculated at the fate level. Their factors reflect the change in pollutant concentration in the environment. Eco-indicator 99 (EI99) uses findings of epidemiology studies to calculate factors at the human effect level. EDIP2003 factors are calculated at human and ecosystem exposure levels, which lie between the fate and effect levels. The reliability of interpretation increases from the fate level to the effect level factors. However, it also introduces higher uncertainty in the factors. The exposure level factors balance the uncertainty in interpretation to the uncertainty in models and parameters (Hauschild and

Table 1 Summary of the features of four characterization methods and the characterization method of this study for photochemical oxidant impacts

Key features	CML2001	EI99	TRACI	EDIP2003	This study
Impact characterization level(s)	Fate level	Human effect level	Fate level	(a) Human exposure (b) Ecosystem exposure	(a) Fate (b) Human exposure (c) Ecosystem exposure (d) Human effect
Category Indicator(s)	ppb O_3	DALY	g of NO_x equivalent	(a) persons·ppm·h (b) m^2·ppm·h	(a) ppb O_3 (b) ppm·persons (c) g O_3 deposited (d) persons (mortality)
Spatial applicability	Europe	Europe	US	Europe	US
Spatial resolution	None in CML2001; low and high NO_x regions in EDIP97	None	State level	Country level	State level
Temporal resolution	None	None	None	Annual	Monthly
Underlying model(s)	Lagrangian EMEP	Lagrangian EMEP, epidemiology studies	EKMA and ASTRAP	RAINS (Lagrangian EMEP)	CAMx, epidemiology studies

Potting 2005). The proposed method generates impact factors at all three levels. This allows flexibility in using the factors appropriate for the intended application and user preferences. Additionally, it provides a comparison among the factors at the three levels.

The category indicators are dependent on the level at which the impact is calculated. CML2001 uses ppb of O_3 produced due to a unit increase in emissions, whereas TRACI uses grams of NO_x equivalents in the receiving environment. EI99 uses DALYs to measure impact on human health. In EDIP2003, persons·ppm·h and m^2·ppm·h are used for human and vegetation exposure, respectively. For the fate level factor, the proposed method uses the change in the average 24 h O_3 concentration (in ppb) for a unit change in emissions. The human exposure factors are calculated in terms of persons·ppm·days, and the ecosystem exposure factors in terms of grams of O_3 deposited per month on vegetated surfaces. The human health effect factors represent the increase in mortality (number of persons) associated with an increase in the short-term O_3 concentration. The finding of an epidemiology study conducted by Bell et al. (2004) is used as the effect model for human health. The concentration–response (C–R) function derived in the study showed that a 10 ppb increase in the daily average O_3 concentration for the previous week increased the daily mortality by 0.52%, nationally.

Three of the four common characterization methods have some form of spatial differentiation. EDIP97 provides different sets of characterization factors for high-NO_x and low-NO_x regimes under European conditions. EDIP2003 provides individual factors for European countries, whereas TRACI factors were calculated for each US state. The proposed model follows TRACI's spatial resolution and uses the US states as the aggregation units. However, none of the common methods consider seasonal differentiation of the factors. EDIP2003 has three sets of factors for three different years representing different economic activities and emission controls. The proposed characterization method provides monthly factors based on the emissions and meteorology scenarios for the year 2001. All methods use photochemical models for characterization. The three European methods rely on the EMEP model, TRACI relies on the combined results of EKMA and ASTRAP simulations, whereas the proposed method uses CAMx as the underlying model.

3.2 Description of the characterization model

A combination of MM5 v3 (http://mmm.ucar.edu/mm5/) (meteorology model), SMOKE v3.2 (http://www.smoke-model.org) (emissions model), and CAMx v4.2 (http://www.camx.com/) (chemistry and transport model) has been used for fate and transport modeling. The models have an

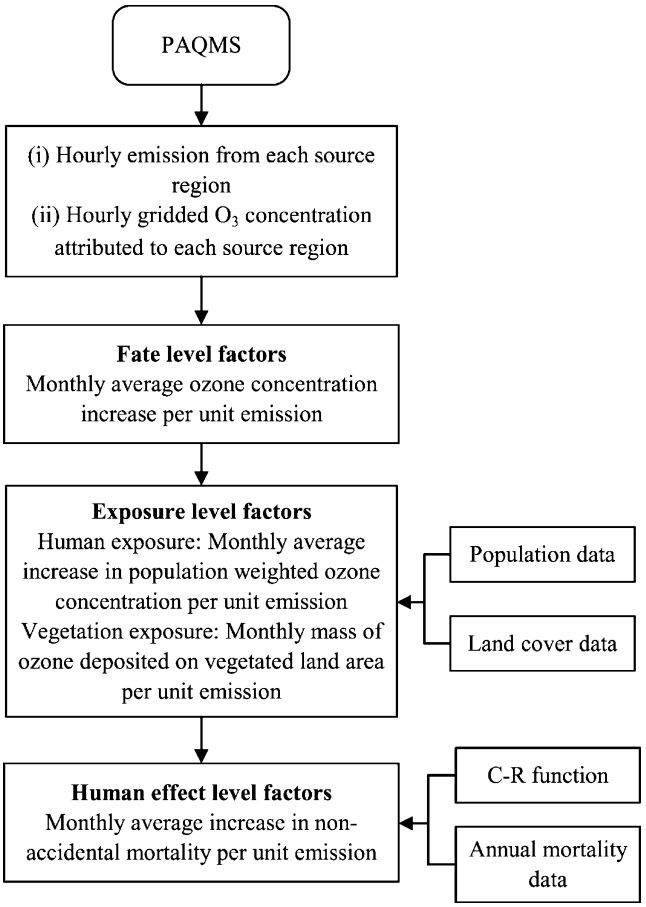

Fig. 2 Summary of the characterization model

hourly time step and a 36×36 km spatial grid resolution. These models have been evaluated and used, individually and in combination, in several previous studies (USEPA 2005a; Tonnesen et al. 2005; Lee et al. 2007). CAMx incorporates Anthropogenic Precursor Culpability Assessment (APCA) as an O_3 source apportionment method. APCA favors the allocation of responsibility to anthropogenic sources over biogenic sources. For instance, when O_3 is formed under VOC limited conditions in the presence of anthropogenic NO_x and biogenic VOC precursors, APCA associates the new O_3 to the anthropogenic NO_x source group (Environ 2006). Source apportionment is performed by using separate tracer species for anthropogenic and biogenic emissions of NO_x and VOCs from each of the 48 coterminous states and Washington DC.

The characterization factors are calculated at the fate (midpoint) level, the exposure level, and at the effect (end point) level. The fate level characterization factor is defined as the amount of O_3 formed per unit emission of a precursor (NO_x or VOC). The quantity of O_3 is not expressed as the absolute mass, but as the average surface level concentration. For a state L, the fate level characterization factor for NO_x for month M with D_M days is calculated as

$$CFFate_{L,NOx,M} = \left(1/D_M \sum_{d=1}^{D_M} 1/n_k \sum_{k=1}^{n_k} [O_3N]_{k,L,d}\right) / \left(1/D_M \sum_{d=1}^{D_M} E_{NOx,L,d}\right) \quad (1)$$

where $[O_3N]_{k,L,d}$ is the 24-h average surface level anthropogenic sourced O_3 tracer (in ppb) in grid cell k for day d, $E_{NOx,L,d}$ (in metric tons, MT) is the anthropogenic NO_x emission from state L on day d. n_k represents the number of cells that contain 95% of the surface O_3 mass present in the domain on day d that is attributed to state L. The remaining 5% of cells have negligible ozone concentrations.

The same method is followed for VOCs, except that the O_3N species are replaced by O_3V species, and the total emissions of VOCs is the reactivity weighted sum of the modeled VOC species, namely the species of the Carbon Bond IV mechanism (CB4) (Environ 2006). The reactivity weighting is used to provide a common base for the VOC mixtures emitted from each state. The MIR of the VOC species, expressed in mass of O_3 formed per unit mass of the species emitted for the CB4 species is presented in the Electronic supplementary material.

The exposure level characterization factor for human health impact due to NO_x is defined as

$$CFHExp_{L,NOx,M} = \left(\sum_{d=1}^{D_M} \sum_{k\in S} \left([O_3N]_{k,L,d} \times p_k\right)\right) / \left(1/D_M \sum_{d=1}^{D_M} E_{NOx,L,d}\right) \quad (2)$$

where p_k is the population of the grid cell, k is derived from the county-level 2001 US Census and S is the entire horizontal modeling domain. Grid resolution population is generated using the population surrogate dataset in SMOKE. The exposure level characterization factor for ecosystem health is based on the predicted flux of O_3 received by the ecosystem. The flux of O_3 is calculated as the total mass of O_3 deposited in each grid cell, in each month, through both dry and wet deposition processes. The contribution of each source to the total deposited mass is determined from the source distribution of the surface-level O_3 concentration in each grid cell and at each time step. Mathematically, this relation for NO_x is

$$CFEExp_{L,NOx,M} = \left(\sum_{d=1}^{D_M} \sum_{k\in SV} \left(O_3Ndep_{k,L,d} \times A_k\right)\right) / \left(1/D_M \sum_{d=1}^{D_M} E_{NOx,L,d}\right) \quad (3)$$

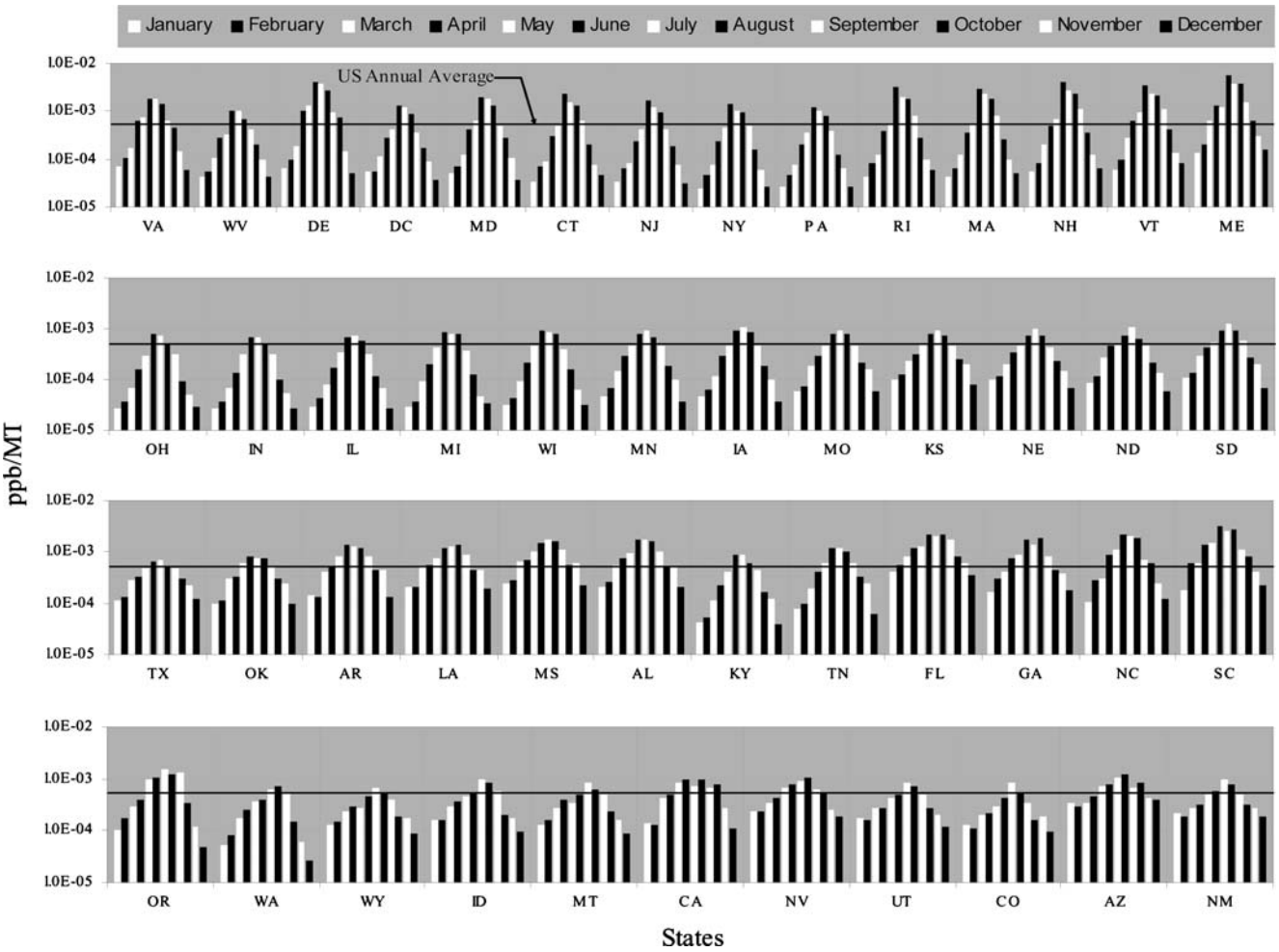

Fig. 3 Monthly fate level characterization factors by state for NO_x emissions

where, SV is the part of the modeling domain which is under vegetation cover, A_k is the area of each grid cell in km^2, and $O_3Ndep_{k,L,d}$ is the mass of O_3 attributed to state L deposited in grid cell k. The areas covered by vegetation have been derived from the US Geological Survey (USGS) land-use/land-cover datasets used in the CAMx model. The exposure level characterization factors for VOCs have similar expressions.

The human health effect level characterization factor for NO_x is based on the C–R function calculated by Bell et al. (2004) and is given as

$$CFHEff_{L,NOx,M} = \left(\sum_{d=1}^{D_M}\sum_{k\in S}\left([O_3N]_{k,L,d}\times\frac{m_k}{365}\times 0.00052\right)\right)\Big/\left(1/D_M\sum_{d=1}^{D_M}E_{NOx,L,d}\right) \quad (4)$$

where m_k is the annual mortality in grid cell k excluding non-resident deaths and deaths resulting from injuries or other external causes, and 0.00052 represents the 0.052% increase in fatalities for an increase in O_3 concentration of 1 ppb. m_k is derived from the county-level annual mortality by distributing it to the corresponding grid cells in proportion to the population distribution. The county-level annual mortality data is obtained from Centers for Disease Control and Prevention's Wide-ranging ONline Data for Epidemiological Research (CDC-WONDER) (http://wonder.cdc.gov). It is the average mortality for the period 1999–2005 for International Classification of Diseases—10 (ICD-10) codes corresponding to non-accidental mortality. The effect level characterization factor for VOC is calculated similarly. A summary of the method is presented in Fig. 2.

4 Results and discussion

Four sets of characterization factors for 48 continental US states and Washington DC for each month for a 1-year period were calculated using the characterization model.

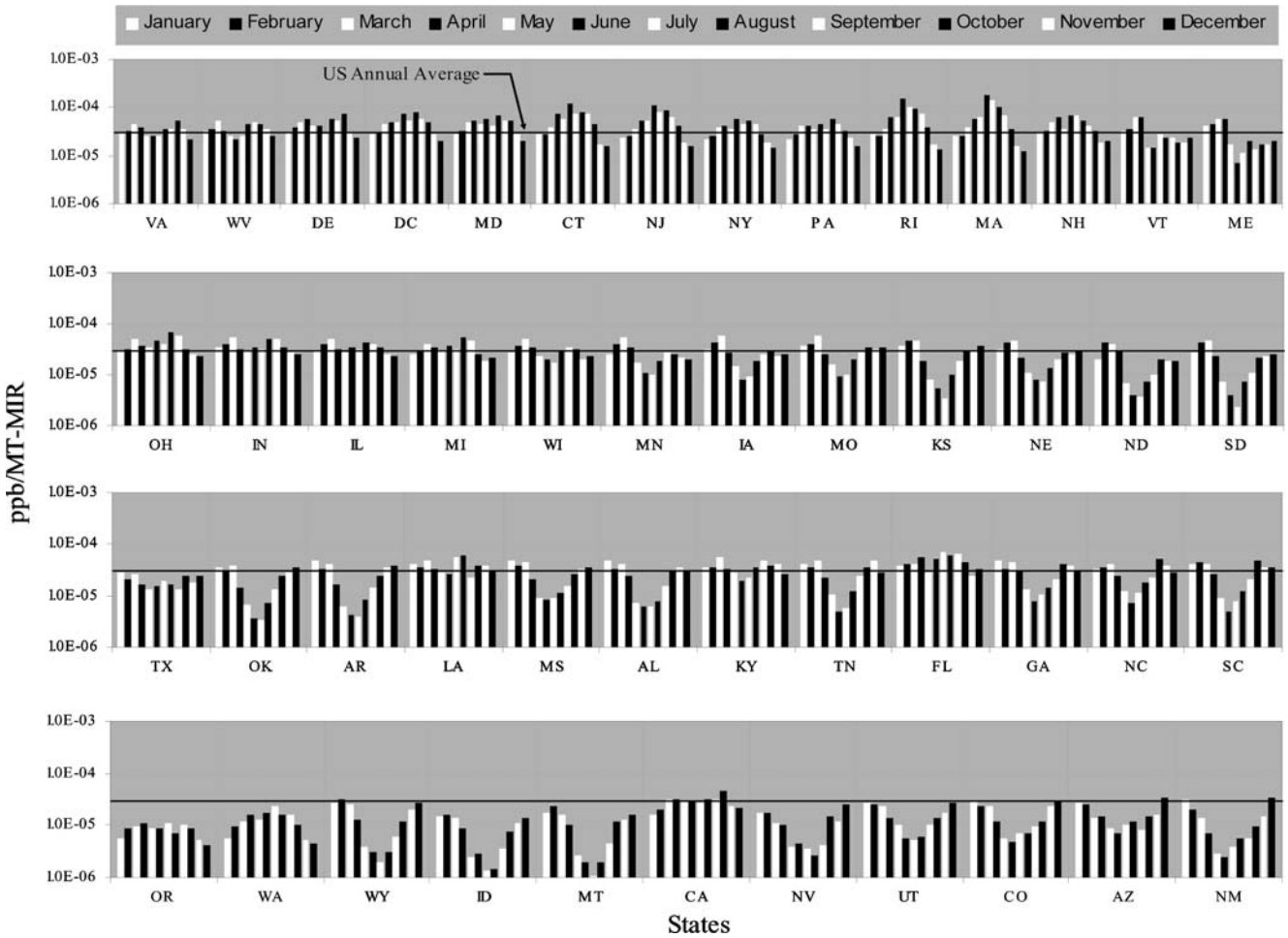

Fig. 4 Monthly fate level characterization factors by state for VOC emissions

The fate level characterization factors for NO_x and VOC are presented in Figs. 3 and 4, respectively. The units of the fate level factors for NO_x and VOC are ppb per MT of emissions, except that, for VOCs, the emissions are weighted with the dimensionless MIR values. The modeled anthropogenic emissions of NO_x and VOC for any given state are nearly equally divided throughout the year. However, the maximum variation in emissions across the states is about two orders of magnitude.

The fate level characterization factors for NO_x exhibit a very high variability across both the months and the states. However, the intra-annual temporal variability is much larger than the spatial variability. Across the US, the characterization factors are the highest in the summer months from June to August and decrease substantially during the winter months. For the northern states, the winter time factors are about two orders of magnitude lower than the summer time factors. The winter time factors are about one order of magnitude lower than the summer time factors for southern states. This is due to the higher temperatures and solar radiation in the southern latitudes during the winter months. On average, the intra-annual variability in VOC factors is smaller compared to the variability for NO_x. The intra-annual variability for VOCs lies within one order of magnitude. The maximum factors are observed in the non-summer months (December to March) in more than half of the states. This effect is due to the strong dependence of biogenic VOC emissions on temperature and solar radiation. During the winter months, the relative contribution of biogenic VOC to the total VOC emissions decreases significantly, especially in the southern states, thus increasing the contribution of anthropogenic VOC to O_3 formation.

The US annual average characterization factors for NO_x and VOC are 5.2E−04 ppb/MT and 3.0E−05 ppb/MT-MIR, respectively. The US annual average is the emission weighted mean of the characterization factors. For an average MIR value of 2.45, the factor for VOC increases to 7.4E−05 ppb/MT of VOC. This implies that 1 MT of anthropogenic NO_x is, on average, seven times more

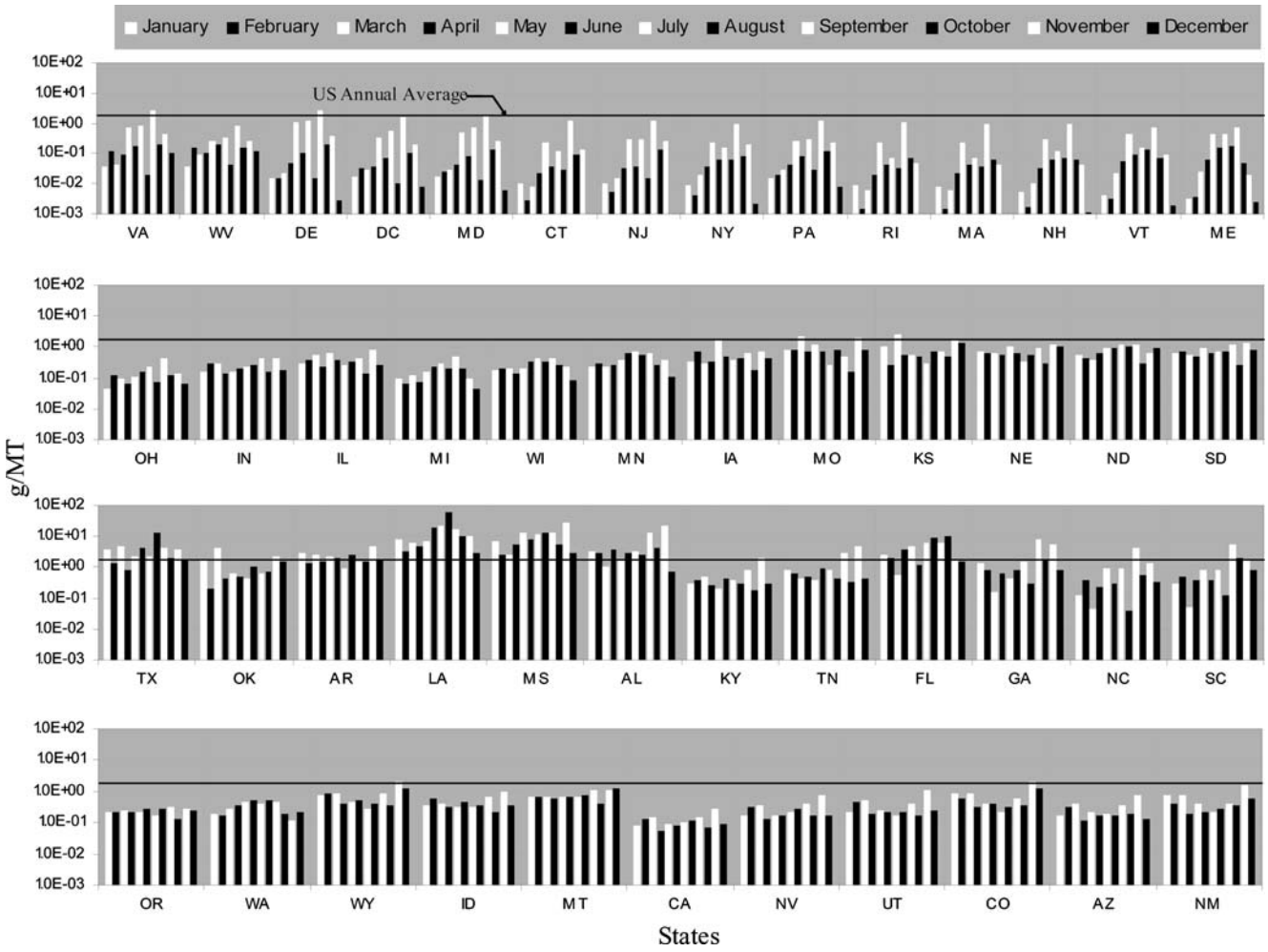

Fig. 5 Monthly ecosystem exposure level factors by state for NO_x

effective than 1 MT of anthropogenic VOC in increasing surface level O_3 concentration. It is important to note that the O_3 attributed to anthropogenic NO_x also includes O_3 formed due to biogenic VOC under VOC limited conditions, which would have normally been attributed to VOC. The overall ratio of the NO_x and VOC characterization factors is slightly higher than the value of 2 assumed in TRACI and obtained in EDIP2003. The MIR value of NO_x, recently calculated by Carter (2007), is about 25, which is about 14 times the MIR for the average VOC mix. However, since the MIR values are calculated under conditions of maximum sensitivity for each of the precursors, they represent the extreme values of the reactivity range. These conditions are not typical of the domain average.

The exposure level characterization factors incorporate the potentially affected human population or ecosystem area due to the ambient O_3 concentrations or O_3 deposition. They are based on the assumption that the actual exposure is directly proportional to the ambient concentration or deposition flux, and it is not significantly affected by other factors. The factors for ecosystem exposure are shown in Figs. 5 and 6. Deposition is dependent on turbulent diffusion in the boundary layer, which is dependent on several other meteorological factors, and the surface characteristics on which the deposition takes place. The ecosystem exposure characterization factors do not follow a pattern similar to the concentration-dependent characterization factors. The maximum variation between the states is more than two orders of magnitude. There is a high level of inter-annual variation among the states, especially in the northeastern states, but the variation does not follow a clear pattern. In the northeastern states, the fluctuation in the months from May to August is about one order of magnitude.

The effect level characterization factors represent mortality increase per unit emission of precursors. The US annual average factors for NO_x and VOC are 4.0E−04 persons/MT and 3.5E−05 persons/MT-MIR, respectively. In other words, a 100 MT increase in daily anthropogenic NO_x

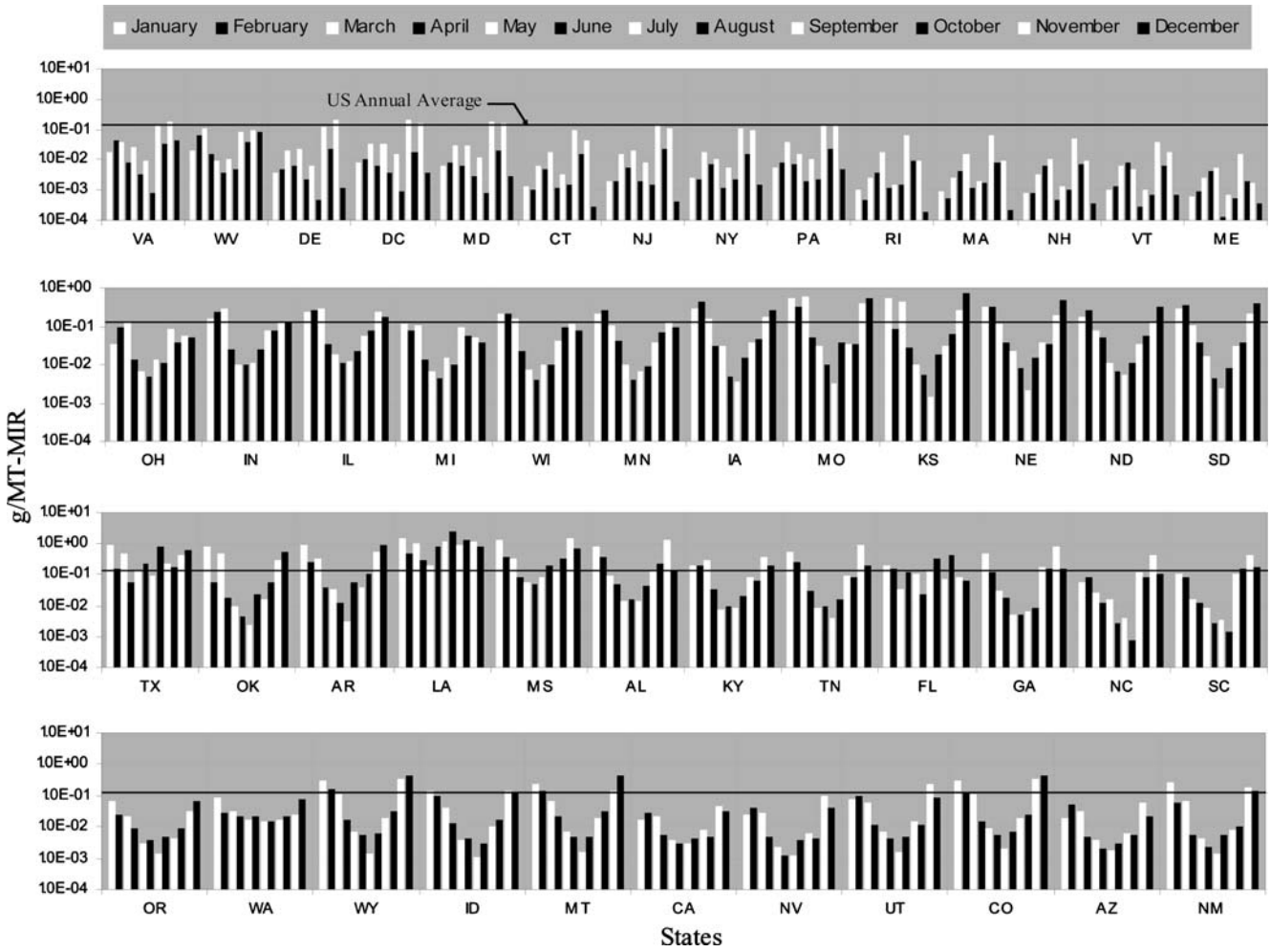

Fig. 6 Monthly ecosystem exposure level factors by state for VOC

emission throughout the year will result in about 14 additional mortalities per year. The pattern of variability in the fate, human exposure, and effect level (concentration-dependent) characterization factors is very similar. A summary of the variation of all the characterization factors is presented in Figs. 7 and 8. The vertical I-shaped bars indicate the maximum and minimum values of the characterization factors normalized to the respective US averages.

In the eastern coastal states, the normalized human exposure and effect level factors are lower than the normalized fate level factors in the winter months. This is mainly due to the continental high pressure forcing winds carrying O_3 and precursors towards the Atlantic Ocean. As expected, most of the sparsely populated western states, such as Nevada, Utah, New Mexico, and Wyoming, have smaller peaks in their human exposure and effect level factors compared to the fate level factors. Conversely, the states where high ozone concentrations affect more densely populated areas, such as California, Ohio, Indiana, and Illinois, have higher peaks in the human exposure and effect level factors.

The concentration-dependent VOC characterization factors are affected significantly by the relative amount of biogenic emissions. States, such as Idaho, Montana, and Wyoming, which have the highest amount of biogenic emissions relative to anthropogenic emissions, have the lowest characterization factors. Conversely, states such as Massachusetts and Rhode Island have the highest concentration-dependent VOC characterization factors. The temporal variability in the concentration-dependent characterization factors for NO_x reflects the variability in meteorology affecting the formation and retention of atmospheric O_3; whereas the temporal variability in factors for VOC is driven by the meteorological processes and land use types that affect the relative contribution of biogenic emissions.

For ecosystem exposure factors, the trend indicates that the characterization factors decrease in the northern states. The highest characterization factors are found in the

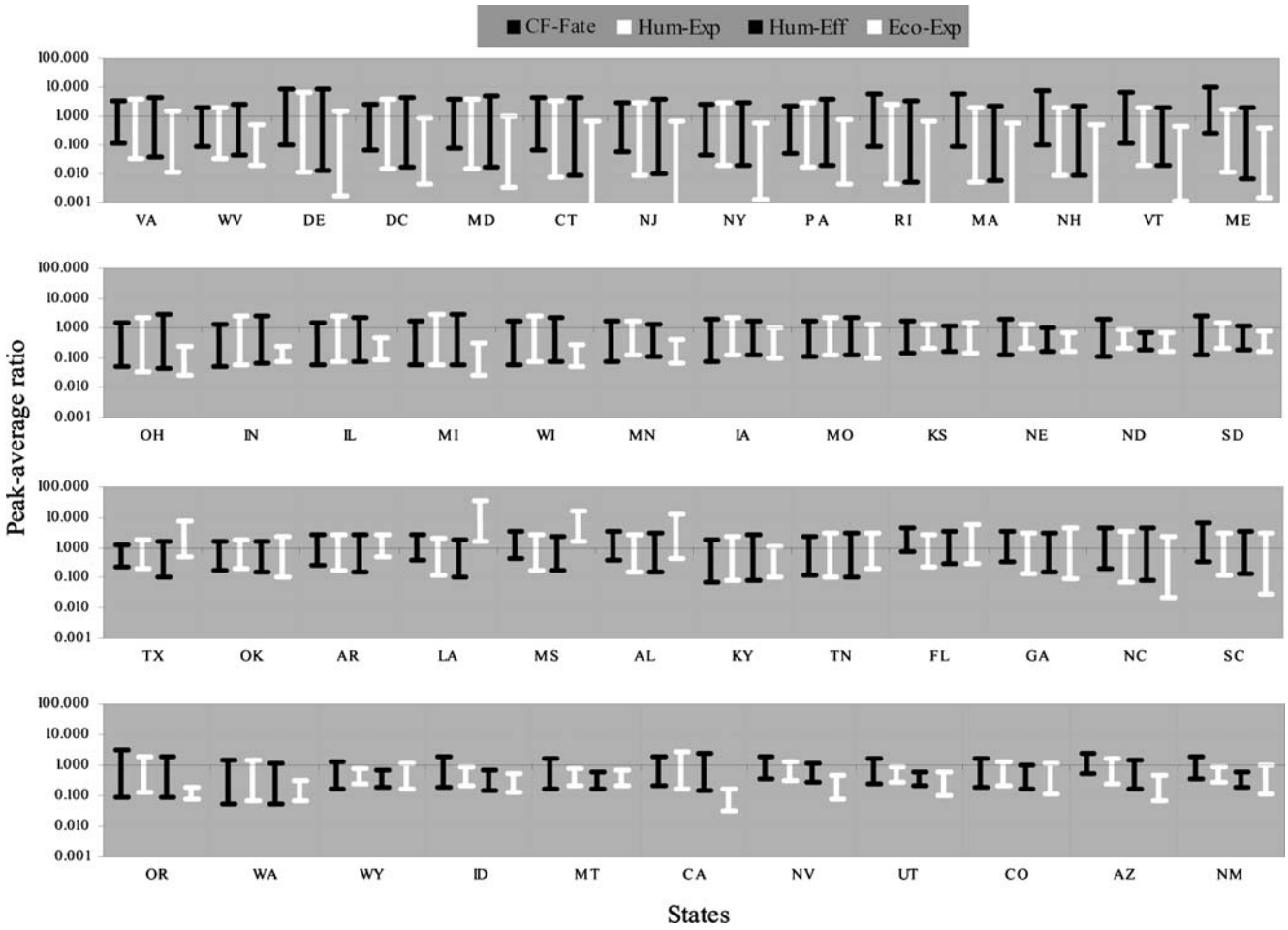

Fig. 7 Normalized maximum and minimum state level characterization factors for NO_x

southern states, such as Louisiana, and characterization factors are lowest in states like Maine, Vermont, and New Hampshire. This is a result of lower vegetation resistance to deposition at higher temperatures and solar radiation. However, for some southern states such as Arizona and Nevada, the characterization factors are relatively low due to the prevalence of semi-arid and desert ecosystems. It is assumed in this study that desert ecosystems do not suffer any significant damage due to O_3 exposure and hence are not considered in the calculation of the exposure factors.

A sensitivity analysis of the characterization factors was performed to assess the variation in the characterization factors due to the annual variation in meteorology and emissions. To test the sensitivity with respect to meteorology, a new set of characterization factors were calculated for the month of July using 2006 meteorology, instead of the 2001 meteorology used in the base case. The emission inputs for this scenario were the same as those used for the base case. The biogenic emissions were not adjusted for the changing meteorological conditions. In a second scenario, a new set of characterization factors was calculated based on a year 2020 emission inventory estimated by the USEPA (2005b). The meteorology of July 2006 was used in this scenario. Biogenic emissions were also recalculated based on the July 2006 meteorology. For both scenarios, the maximum change in the concentration-dependent characterization factors was a factor of 2, and a factor of 3.5 for ecosystem exposure factors. Therefore, the spatial variation in the characterization factors is more than one order of magnitude higher than the variation due to variability in meteorological conditions or emissions. Despite the uncertainty in the state level characterization factors due to the model inputs used in this study, a higher uncertainty is introduced in LCIA by neglecting the spatial variability of O_3 formation.

5 Conclusions

The photochemical oxidant impact characterization models of four common LCIA methods (CML2001 and EDIP97,

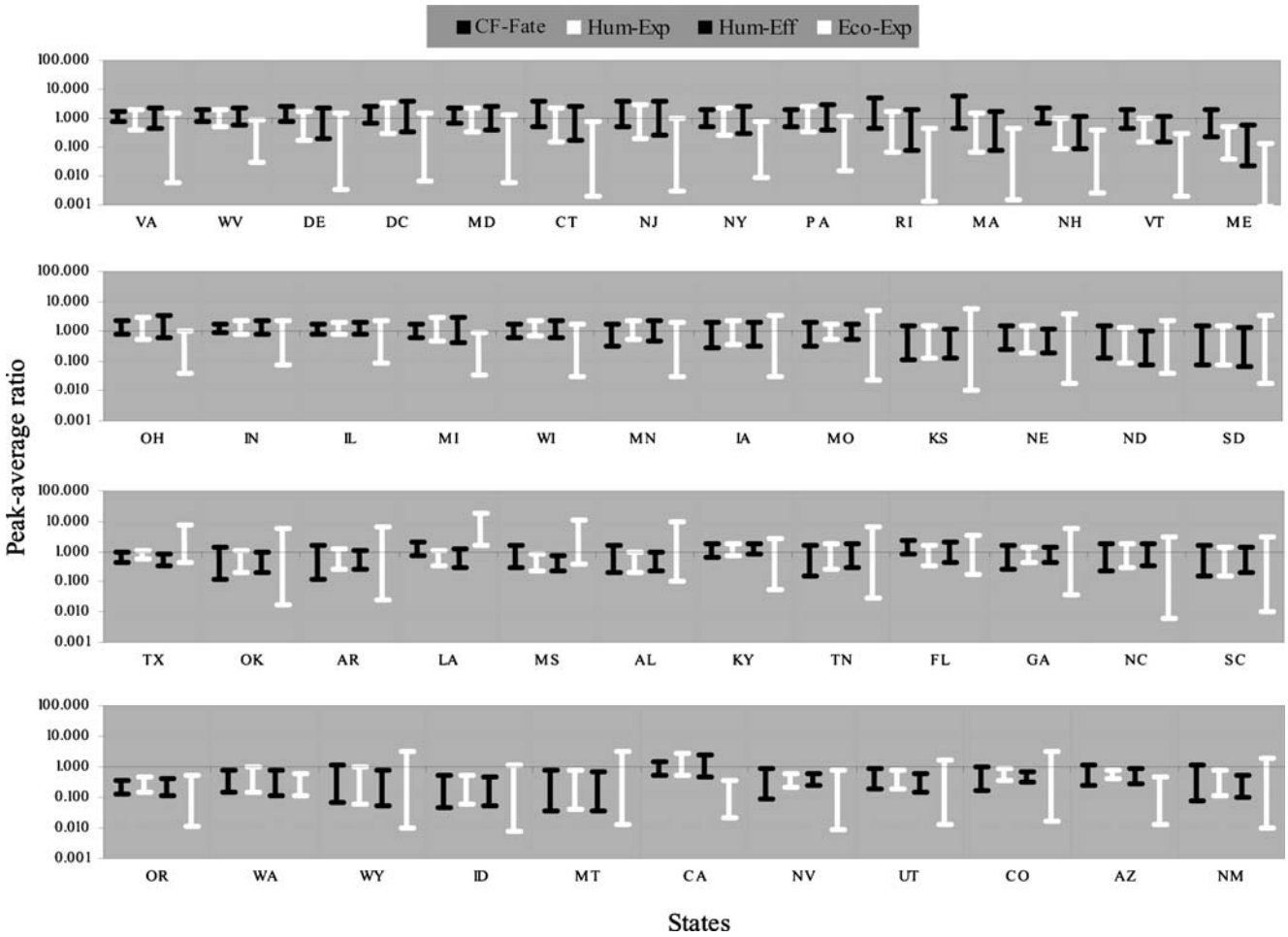

Fig. 8 Normalized maximum and minimum state level characterization factors for VOC

Eco-indicator 99, TRACI, and EDIP2003) were reviewed. They were compared with respect to the level at which the impacts are calculated, the spatial and temporal resolution, the spatial applicability, and the underlying photochemical models. It was found that each of the methods had limitations in at least one of the aspects. For example, although TRACI incorporates spatial differentiation at the state level, the recent advances in photochemical modeling allow improvement in the underlying models used in TRACI.

A new characterization method is proposed that incorporates spatial and temporal resolution, and calculates characterization at the fate, human and ecosystem exposure, and human effect levels. Annual hourly simulation of the United States using the MM5-SMOKE-CAMx photochemical air quality modeling system was performed to determine the variability in the factors due to the location and time of emission. The proposed method considered NO_x and VOC as the important photochemical precursors, and O_3 as the indicator oxidant species. Characterization factors for anthropogenic NO_x and VOC were developed for each of the 48 continental states and Washington DC for each month of a year.

A very high spatial and temporal variability was seen in the characterization factors. For states, the difference between the maximum and minimum fate level and human exposure and effect level characterization factors for NO_x was between one and two orders of magnitude. For any given month, the maximum difference in the characterization factors across the spatial domain was close to one order of magnitude. The time at which the emissions occur has a stronger influence on the characterization factors than their location. The concentration-dependent VOC characterization factors showed relatively less variation overall, although the variation was close to two orders of magnitude for a few states. The intra-annual variation for most of the states was within one order of magnitude. Ecosystem exposure also showed a very high spatial and temporal variation. It was more than three orders of magnitude for some states. No clear temporal pattern emerged for the ecosystem NO_x characterization

factors because of the dependence of the deposition processes on several meteorological factors. For VOCs, a pattern similar to the concentration-dependent factors was seen. Overall, no significant change in variability is seen in moving from fate level factors to human exposure or human effect level factors. However, the ecosystem exposure level factors have a variability of one order of magnitude higher both temporally and spatially compared to the other factors. The pattern of variability also differs from the human exposure factors due to the dissimilarity in the effect mechanism.

Spatial and temporal differentiation takes into account the fate and transport of the pollutant and the exposure of and effect on the sensitive human population or ecosystem. Adequate resolution for seasonal and regional processes like photochemical O_3 formation is important to reduce the uncertainty in impact assessment and improve decision-making power. Spatial and temporal differentiation of the characterization factors has a limited benefit if the life cycle inventory is aggregated. An emphasis on incorporating some form of spatial and temporal information within standard LCI databases, and using adequately resolved characterization factors will greatly increase the fidelity of a standard LCA.

References

Andersson-Sköld Y, Grennfelt P, Pliejel K (1992) Photochemical ozone creation potentials: a study of different concepts. J Air Waste Manag Assoc 42(9):1152–1158

Bare JC, Norris GA, Pennington DW, McKone T (2003) TRACI: The Tool for the Reduction and Assessment of Chemical and other environmental Impacts. J Ind Ecol 6(3):49–78

Bell MI, McDermott A, Zeger SL, Samet JM, Dominici F (2004) Ozone and short-term mortality in 95 US urban communities, 1987–2000. JAMA 292(19):2372–2378

Bellekom S, Potting J, Benders R (2006) Feasibility of applying site-dependent impact assessment of acidification in LCA. Int J LCA 11(6):417–424

Carter WPL (1998) Updated maximum incremental reactivity scale for regulatory applications. Preliminary report to California Air Resource Board. August 6. http://pah.cert.ucr.edu/~carter/bycarter.htm, accessed 21.7.2007

Carter WPL (2007) Development of the SAPRC-07 chemical mechanism and updated ozone reactivity scales. Final report to California Air Resource Board. August 31. http://pah.cert.ucr.edu/~carter/SAPRC/, accessed Sept. 15, 2007

Derwent RG, Jenkin ME (1991) Hydrocarbons and the long range transport of ozone and PAN across Europe. Atmos Env 25A (8):1661–1678

Derwent RG, Jenkin ME, Saunders SM (1996) Photochemical ozone creation potential for a large number of reactive hydrocarbons under European conditions. Atmos Env 30(2):181–199

Derwent RG, Jenkin ME, Saunders SM, Pilling MJ (2001) Characterization of the reactivities of volatile organic compounds using a master chemical mechanism. J Air Waste Manag Assoc 51 (5):699–707

Environ International Corporation (2006) CAMx user's guide v4.40. http://www.camx.com/publ/index.php, accessed March 4, 2007

Goedkoop M, Spriensma R (2001) The eco-indicator 99 A damage oriented method for life cycle impact assessment. PRé Consultants, Amersfoort

Guinée JB, Gorrée M, Heijungs R, Huppes G, Kleijn R, de Koning A, van Oers L, Sleeswijk AW, Suh S, Udo de Haes HA, de Bruijn H, van Duin R, Huijbregts MAJ (2002) Handbook on Life Cycle Assessment: Operational Guide to the ISO Standards. Kluwer, Dordrecht

Haushild M, Wenzel H (1998) Environmental assessment of products vol. 2—scientific background. Kluwer, Boston

Hauschild M, Potting J (2005) Spatial differentiation in life cycle impact assessment—the EDIP2003 methodology. Environmental News No. 80. Danish Environmental Protection Agency, Copenhagen, Denmark

Heyes C, Schopp W, Amann M, Unger S (1996) A reduced form model to predict long term ozone concentrations in Europe. Interim report WP-96-12/December. International Institute for Applied Systems Analysis, Laxenburg, Austria

Heyes C, Schopp W, Amann M, Bertok I, Cofala J, Gyarfas F, Klimont Z, Makowski M, Shibayev S (1997) A model for optimizing strategies for controlling ground level ozone in Europe. Interim report IR-97-002/January 1997. International Institute for Applied Systems Analysis, Laxenburg

Hofstetter P (1998) Perspectives in life cycle impact assessment: a structured approach to combine models of the technosphere, ecosphere, and valuesphere. Kluwer, Boston

Kasibhatla P, Chameides WL, Saylor RD, Olerud D (1998) Relationships between regional ozone pollution and emissions of nitrogen oxides in the eastern United States. J Geophys Res 103 (D17):22663–22669

Lee SM, Fernando HJS, Clarke-Grossman S (2007) MM5-SMOKE-CMAQ as a modeling tool for the 8-h ozone regulatory enforcement: application to the state of Arizona. Environ Model Assessment 12:63–74

Norris GA (2003) Impact characterization in the Tool for the Reduction and Assessment of Chemical and other environmental Impacts. J Ind Ecol 6(3–4):79–101

Pennington DW, Potting J, Finnveden G, Lindeijer E, Jolliet O, Rydberg T, Rebitzer G (2004) Life cycle assessment part 2: current impact assessment practice. Env Int 30:721–739

Potting J, Haushild M (2005) Background for spatial differentiation in life cycle impact assessment—the EDIP2003 methodology. Environmental Project No. 996. Danish Environmental Protection Agency, Copenhagen, Denmark. http://www2.mst.dk/Udgiv/publications/2005/87-7614-581-6/html/indhold_eng.htm, accessed March 10, 2007

Potting J, Hauschild M (2006) Spatial differentiation in life cycle impact assessment. Int J LCA 11(Sp. Iss. 1):11–13

Russell AG (1997) Regional photochemical air quality modeling: model formulations, history, and state of science. Annu Rev Energy Environ 22:537–588

Shannon JD (1991) A model of regional long-term average sulfur atmospheric pollution, surface removal, and net horizontal flux. Atmos Environ 15(5):689–701

Shah VP (2008) A characterization model with spatial and temporal resolution for life cycle impact assessment of photochemical precursors in the United States. MS Thesis. University of Pittsburgh, Pittsburgh PA, USA

Simpson D (1993) Photochemical model calculations over Europe for two extended summer periods: 1985 and 1989. Model

results and comparison with observations. Atmos Env 27A (6):921–943

Tonnesen G, Wang Z, Omary M, Chien CJ, Morris R, Mansell G (2005) Final report for the Western Regional Air Partnership (WRAP) Regional Modeling Center (RMC) for the project period March 1, 2004 through February 28, 2005. http://pah.cert.ucr.edu/aqm/308/reports/final, accessed Sept. 18, 2007

Udo de Haes HA, Jolliet O, Finnveden G, Goedkoop M, Hauschild M, Hertwich E, Hofstetter P, Jolliet O, Klöpffer W, Krewitt W, Lindeijer E, Muller-Wank R, Olsen I, Pennington D, Potting J, Steen B (2002) Life cycle impact assessment: striving towards best practice. SETAC, Pensacola

USEPA (2005a) Technical support document for the final Clean Air Interstate Rule—air quality modeling. http://www.epa.gov/scram001/reportsindex.htm, accessed Sept. 8, 2007

USEPA (2005b) Regulatory impact analysis for the final Clean Air Interstate Rule. EPA-452/R-05-002. http://www.epa.gov/scram001/reportsindex.htm, accessed Jan. 18, 2008